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Thermal behavior and characteristics of fired geopolymers produced from local Cameroonian metakaolin

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Abstract

The thermal behavior along with certain characteristics of geopolymers produced from local Cameroonian metakaolin and heated up to 1000 °C were examined. Geopolymers fired up to 900 °C had the same physical aspect as initial ones and those fired at 1000 °C warped, were glazed and blistered. The TG showed elimination of water according to two stages. The dilatometric curves of preheated samples showed shrinkage between 90 and 250 °C followed by expansion and sintering. The samples heated up to 700 °C were amorphous and new crystalline phases appeared around 900 °C. The microstructure of geopolymers heated between 300 and 900 °C showed progressive disruption and the linear shrinkage increased. The water absorption of the samples fired up to 700 °C increased slightly and tremendously around 900 °C. A drastic decrease of compressive strength was observed with the samples fired between 300 and 900 °C. Hence, the characteristics of geopolymers lessened with elimination of the water which forms hydration spheres around the compensating cations (Na^+) opposed to tetrahedral groups AlO_4^- along with transformation of amorphous phase.

Keywords: Metakaolin; Geopolymers; Characteristics; Thermal behavior; Amorphous phase

1. Introduction

Geopolymers are materials that consist of polymeric silicon–oxygen–aluminum framework with silicon and aluminum tetrahedral alternately linked together in three directions by sharing all the oxygen atoms. The negative charge of aluminum in IV-fold coordination is compensated by cations such as Na^+, K^+ [1]. These materials can be considered as being made up of non-crystalline network which is close to that of zeolites [2]. According to certain authors [3,4] geopolymers are generally endowed with thermal stability which depends on characteristics such as the charge of compensating cation, the ratio of Si/Al and the phases which they are found [5,6]. When geopolymers are heated at high temperature, there are certain modifications such as change of dimension due to thermal shrinkage and sintering, formation of new T–O–T bonds or phases whose thermal stability is more or less important. Several studies on heating of metakaolin-based geopolymers, fly ash-based-geopolymers or certain by-products-based geopolymers at high temperatures have been carried out including determination of new crystalline phases [4,7,8], change of physical and mechanical properties [6,9–11], modification of microstructure [12,13], etc. It has been observed that the highest heating temperature experimented is more or less variable and depends on the nature of the raw aluminosilicate material and composition of alkaline medium used for the synthesis of geopolymers [14]. As for metakaolin-based geopolymers, serious damage is noticeable around 800–850 °C [8,14].

The objective of this work is to investigate the thermal behavior and to determine certain chararacteristics of fired products of geopolymers produced by using local Cameroonian metakaolin as aluminosilicate. This study focuses particularly on the fate of water and amorphous phase of geopolymers under elevated temperatures. With this in mind, the samples were exposed between ambient temperature and

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1000 °C. The resulted products were characterized via visual appearance, thermal analysis (DSC, TG and dilatometry), X-ray diffractometry, Fourier transform infrared spectrometry, scanning electron microscopy as well as determination of certain physical and mechanical properties (thermal shrinkage, water absorption and compressive strength).

2. Materials and methods

2.1. Materials

The metakaolin was obtained from kaolin provided by the group Nubru Holding which is involved in the valorization of certain local raw materials in Cameroon. Before to be used, the kaolin was enriched with kaolinite via the sedimentometry process based on Stockes′ law [15]. The clay fraction obtained was dried at 105 °C until its weight became constant then it was ground and sifted through a sieve of mesh 80 μm followed by calcination at 700 °C [16] for 10 h at a heating rate of 5 °C/min in a programmable electric furnace (Nabertherm, Mod. LH 60/14). The diffractograms of both the clay fraction and the metakaolin are given in Fig. 1. The chemical composition (%wt) of the metakaolin was as follows: SiO_2 (51.46), Al_2O_3 (41.71), Fe_2O_3 (2.66), CaO (0.10), Na_2O (0.39), K_2O (0.70), TiO_2 (0.95) and LOI, 2.03. The specific surface area of metakaolin determined according to BET method was $20.88 \pm 0.06\ m^2/g$ and the particle size distribution was as follows: $d_{10}=5.65$ μm, $d_{50}=30.75$ μm and $d_{90}=70.01$ μm. The alkaline solution was obtained via mixing of a solution of sodium hydroxide (12 M) and sodium silicate made up of 28.7 wt% of SiO_2, 8.9 wt% of Na_2O, 62.4 wt% of H_2O and SiO_2/Na_2O molar ratio of 3.3.

2.2. Paste samples preparation and analytical techniques

To get the geopolymer paste samples, metakaolin powder and alkaline solution were mixed according to the following molar ratios: $SiO_2/Al_2O_3=3.4$, $Na_2O/Al_2O_3=0.8$ and $H_2O/Na_2O=15.1$. The mixture was homogenized in a Hobart mixer (M & O, model N50-G) for 10 min and the fresh paste poured in PVC molds. Once molded, the pastes were vibrated for 10 min on an electrical vibrating table (M & O, type 202, N°106) to remove entrapped air bubbles. Three types of samples were made i.e. large cylinders (diameter: 30 mm and height: 60 mm), small cylinders (diameter: 18 mm and height: 20 mm) and parallelepipeds ($7 \times 7 \times 65\ mm^3$) and were covered with polyethylene film and stored at room temperature (25 ± 3 °C) for 24 h before demoulding. The large cylinder samples were used for visual observation and determination of thermal shrinkage and compressive strength. The water absorption and scanning electron microscopy were performed using the small cylinder samples while the dilatometric analysis was done on the parallelepiped ones. After 28 days of storage at ambient temperature (25 ± 3 °C) of the laboratory, the samples were either cured at 90 °C (24 h in an oven) or heated in a programmable electric furnace (Nabertherm, Mod. LH 60/14) at heating rate of 5 °C/min and soaking time of 2 h at the following temperatures: 300, 500, 700, 900 and 1000 °C. The determination of thermal shrinkage was performed using a vernier calliper and the compressive strength with the help of a hydro-electric press (M & O, type 11.50, N°21) which operates at an average rate of 3 mm/min. The determination of water absorption was carried out according to the ASTM C 373-88 standard [17]. The thermal analysis (DSC and TG) were done using a NETZSCH STA-429 at heating rate of 20 °C/min up to 1200 °C in air. The dilatometric analysis was performed with a mechanic dilatometer (Adamel–Lomargy, model DM-15). Fourier transform infrared spectroscopy was carried out on powders of geopolymer using a Bruker Alpha-P in absorbance mode (interval of wave number ranging was 4000–400 cm^{-1}). Scanning Electron Microscopy (SEM) was carried out using a Philip XL 30 EM. The crystalline phases were determined using X-ray diffractometry with the aid of a Philip PW 3050/60 diffractometer, operating by reflexion of $K_{\alpha 1}$ radiation of Cu.

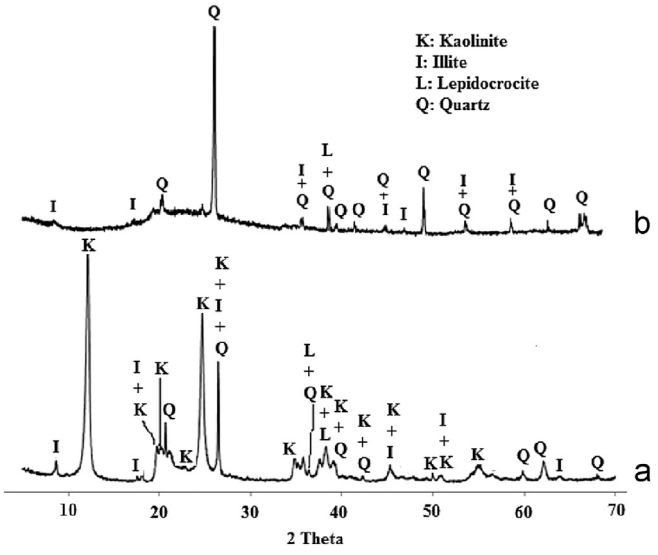

Fig. 1. X-ray diffractograms of kaolin (a) and metakaolin (b).

3. Results and discussion

3.1. Appearance, phase composition and microstructure before and after thermal treatment of geopolymers

After demoulding, the geopolymer cylinders maintained at room temperature, at 90 °C or heated at 900 °C had the same physical appearance (Fig. 2a). On the contrary, large and small cylinder geopolymers heated at 1000 °C warped and were glazed, blistered and presented cracks (Fig. 2b). FTIR spectra (Fig. 3) showed that unlike the metakaolin and the geopolymer heated at 900 °C, the samples cured at room temperature or heated at 90, 300 and 500 °C showed absorption bands at 3400–3450 cm^{-1} and at 1640–1650 cm^{-1} and their intensities decreased with increase in temperature. These bands correspond respectively to deformation vibration of H–O–H bonds and elongation of O–H groups of molecules of water [18–21]. Hence, though heated at 500 °C, not all the water involved in

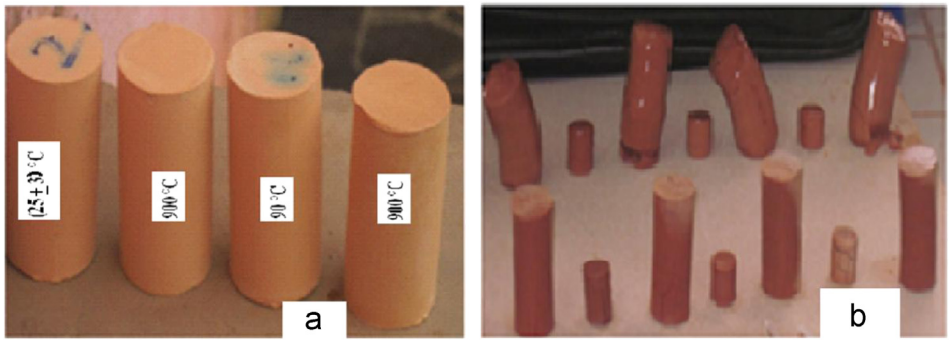

Fig. 2. Visual aspect of the geopolymers maintained at ambient temperature, 90 °C, 900 °C (2.a) or heated at 1000 °C (2.b).

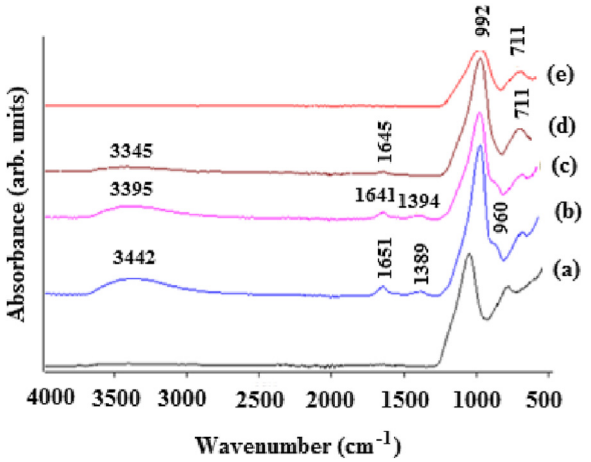

Fig. 3. FTIR spectra of metakaolin (a) and of the geopolymers cured at 25 °C (b); 90 °C (c); 500 °C (d); and 900 °C (e).

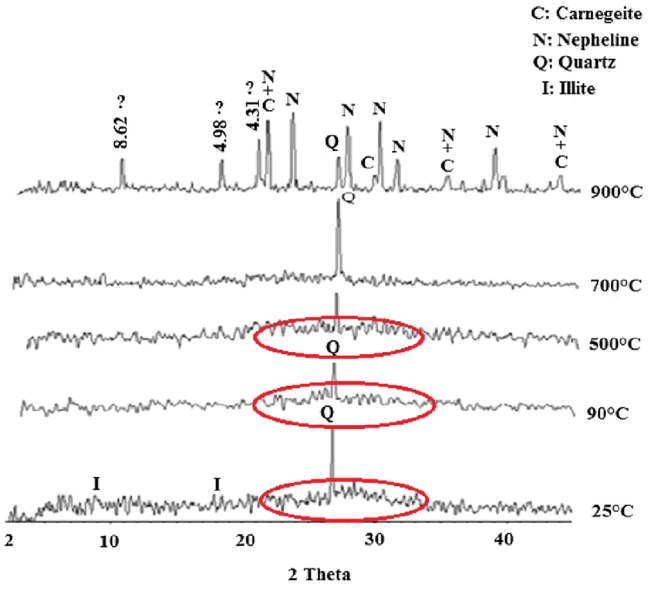

Fig. 4. X-ray diffractograms of the geopolymers.

the process of preparation of geopolymer was used up implying that the water was progressively eliminated with increase in temperature. The absorption band at 1390–1410 cm^{-1} corresponds to the asymmetrical vibration of Si–O or Al–O bonds [22] which disappeared with increase in temperature. The absorption band located around 992–1000 cm^{-1} (Fig. 3b–d) corresponds to vibrations of symmetric and asymmetric elongation of Si–O–Si and Si–O–Al bonds and emphasizes a major fingerprint of geopolymer matrix [23]. Near to the previous absorption band, FTIR spectra of the geopolymers cured at 25 and at 90 °C (Fig. 3b and c) exhibit a narrow shoulder around 960 cm^{-1} which corresponds to vibration of elongation of the Si–O bond [22]. The existence of weak band at 711 cm^{-1} is assigned to the symmetric stretching of Si–O–Si and Si–O–Al bonds [22]. When the geopolymers were maintained at room temperature or fired up to 700 °C, quartz was the main crystalline phase observed (Fig. 4). The diffused halo peak with 2θ between 20° and 30° is characteristic of amorphous phase present in geopolymer and its intensity decreased with increase in temperature. This peak was no more observed when geopolymers were heated at 700 °C (Fig. 4). As for the geopolymer heated at 900 °C, in addition to quartz, new crystalline phases (nepheline and carnegeite) plus other peaks which could not be assigned were observed. SEM micrographs (Fig. 5) showed that the microstructure was made up of interlocked thin layers. Despite the presence of pores, the microstructure of the geopolymer cured at 90 °C showed good cohesion. Conversely, with increase in temperature between 300 and 900 °C, the microstructure of geopolymers showed layers that were progressively detached each other. This virtual peeling phenomenon was more emphasized at 900 °C, which indicated deterioration of geopolymers via crystallization of the amorphous phase (Fig. 4).

3.2. Thermal analysis

The thermal analysis (TG and DSC) of geopolymer initially cured at ambient temperature is shown in Fig. 6. The TG curve showed a decrease in mass which indicated elimination of water contained in the geopolymer. This decrease stopped around 750 °C and represented about 16.5 wt% of the geopolymer. Water was eliminated at a high rate around 100 and 250 °C which may indicate a two stage process. This process was also emphasized by the appearance of a shoulder on the DSC curve. Elsewhere, the dilatometric curves of the geopolymers preheated at 90, 300, 500 and 700 °C (Fig. 7) were each characterized by shrinkage between 90 and 250 °C which expressed among other things elimination of water whose

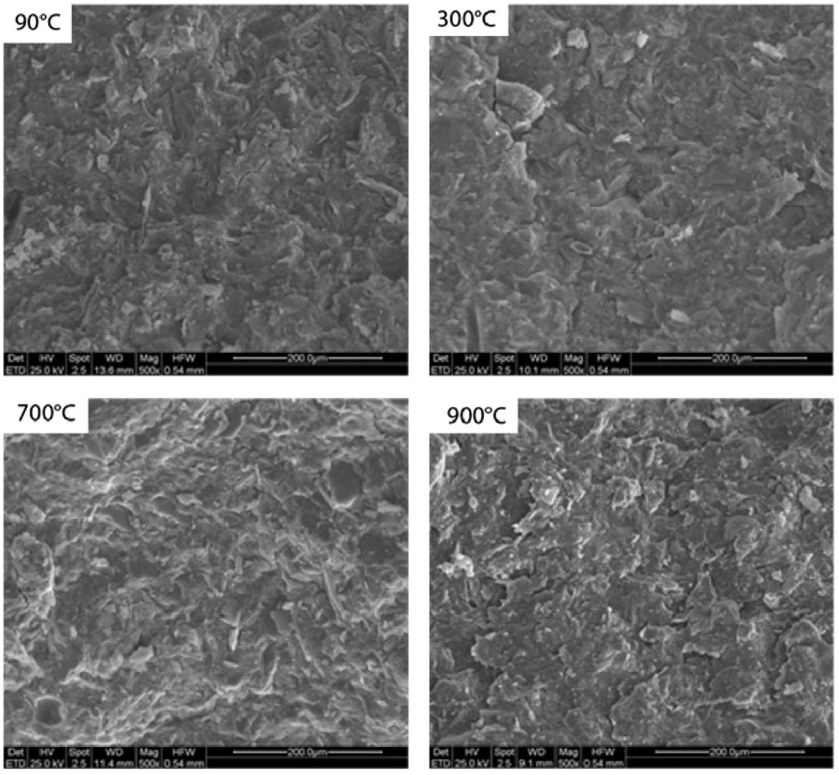

Fig. 5. Micrographs of the geopolymers.

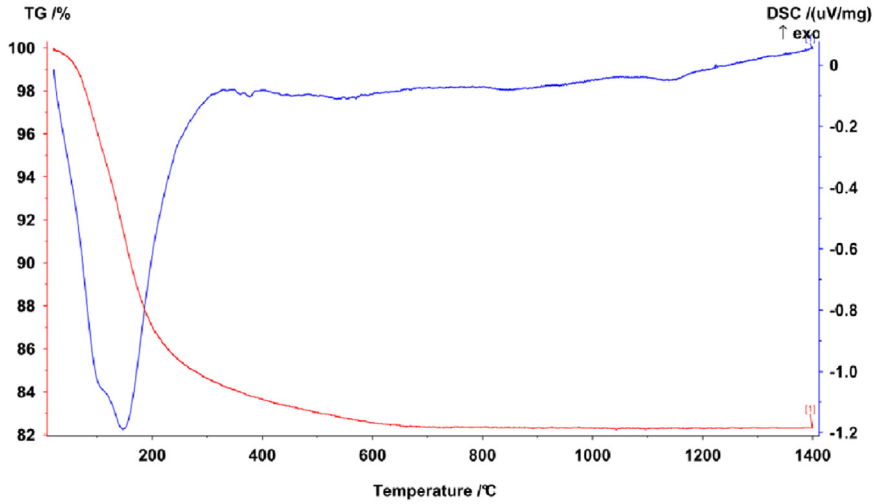

Fig. 6. Thermal behavior of metakaolin-based geopolymer initially cured at ambient temperature.

magnitude decreased progressively with increase in preheating temperature. Metakaolin-based geopolymers are known to contain abundant pores [24] and when submitted to heat, three types of water are generally eliminated: "free water" up to 125 °C, "interstitial water" between 125 and 250 °C and "hydroxyl water" between 250 and 750 °C which forms hydration spheres around the compensating ions Na^+ opposed to tetrahedral groups AlO_4^- in the structure of geopolymer gel [25]. The TG result (Fig. 6) has shown that when heating geopolymer, the water was progressively eliminated according to two stages: "free water" and "interstitial water" (first stage) and "hydroxyl water" (second stage). There is more energy required for the elimination of water of the second stage than the first. In fact, in addition to the energy needed to expel molecules of water from the geopolymer, there is supplementary energy required to break off hydrogen bonds between molecules of water and Na^+ ions which compensate the negative charge of AlO_4^- groups in the structure of geopolymer gel. In each sample preheated between 300 and 700 °C, the dilatometric analysis showed the presence of shrinkage between 90 and 250 °C (Fig. 7b–d). For this particular case, the shrinkage resulted from elimination of a part of water molecules in the second stage. This resulted from the fact that during the preheating of geopolymer between 300 and 700 °C,

certain molecules of water at the second stage remained located in the pores of the heated material. Hence, the remaining molecules of water at the second stage present in the pores of the preheated product behaved as those of the first stage during the dilatometric analysis. It was also interesting to observe that when metakaolin-based geopolymers were submitted to the dilatometric analysis, the shrinkage (Fig. 7) which accompanies the main sintering is generally observed between 700 and 800 °C [26,27].

3.3. Thermal shrinkage, water absorption and compressive strength

The thermal shrinkage of geopolymers aged of 28 days increased with increase in heating temperature (Fig. 8). For the geopolymers cured at ambient temperature and at 90 °C, the thermal shrinkage was as a result of elimination of water during the polycondensation stage. This process was accompanied with the creation of capillary tensions which brought the particles closer [28] and produced water whose amount increased with increase in temperature as shown by the TG (Fig. 6). As for the geopolymers heated between 300 and 700 °C, the dilatometric analysis (Fig. 7b–d) showed the existence of shrinkage which correlated well with the increase of thermal shrinkage in Fig. 8. When the geopolymer was heated at 900 °C, there was a high increase of thermal shrinkage which resulted likely from the formation of new crystalline phases (Fig. 4). The water absorption of the geopolymers maintained between 25 and 700 °C did not vary noticeably (Fig. 9) because of low increase of pores and cracks as shown by the micrographs (Fig. 5). Conversely, the micrograph of geopolymer heated at 900 °C showed a considerable amount of peeling which generated cracks that were responsible for the high water absorption. The compressive strength of the geopolymers cured at ambient temperature and at 90 °C increased appreciably contrary to those heated between 300 and 900 °C (Fig. 10). In fact, the synthesis of geopolymers is generally carried out between room temperature and 90 °C [29,30] which leads to products whose microstructure is compact enough and with high compressive strength [30]. The microstructure of geopolymers heated between 300 and 900 °C was progressively modified because of elimination of "hydroxyl water" [25] along with decrease of amount of amorphous phase (hump between 20° and 30° in Fig. 4) which led to the decrease of compressive strength (Fig. 10). In Portland cement pastes, compressive strength is already reduced of above 50% when exposed to temperatures between 400 and 500 °C [31]. Hence even though there is decrease of compressive strength when

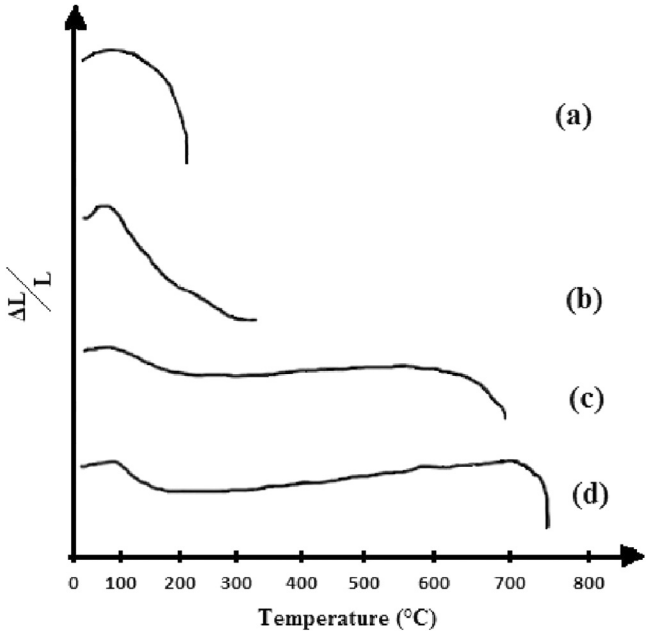

Fig. 7. Dilatometric curves of preheated geopolymers (90 °C (a); 300 °C (b); 500 °C (c); and 700 °C (d)).

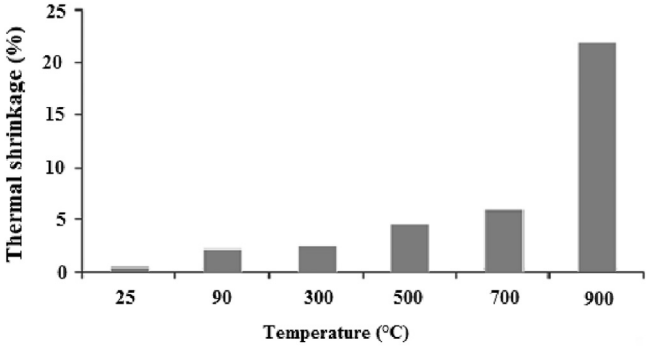

Fig. 8. Thermal shrinkage of the geopolymers.

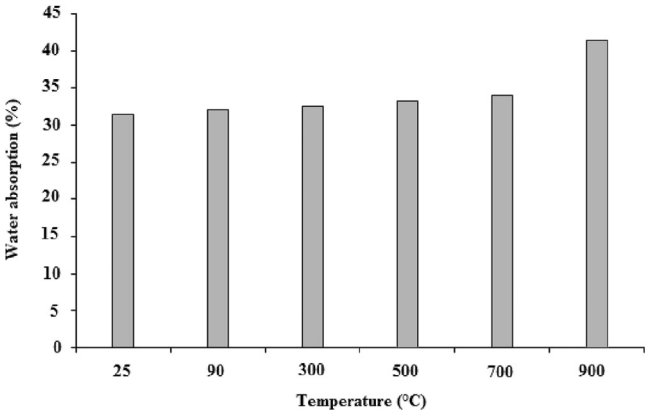

Fig. 9. Water absorption of the geopolymers.

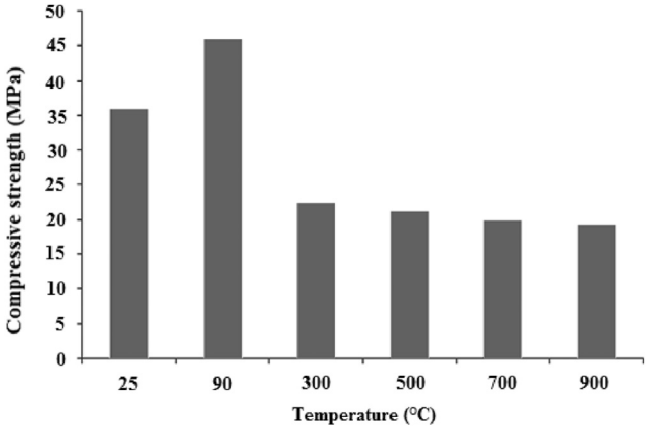

Fig. 10. Compressive strength of the geopolymers.

exposed to elevated temperatures, the comparison with respect to Portland cement shows that metakaolin-based geopolymers remain valuable.

4. Conclusion

The thermal behavior of geopolymers produced from local Cameroonian metakaolin as aluminosilicate between ambient temperature and 1000 °C was characterized by elimination of water up to 750 °C followed by sintering and formation of new crystalline phases. Water was eliminated according to two stages. The first stage concerned "free water" and "interstitial water" and the second stage corresponded to "structural water" which surrounds Na^+ ions that compensate the negative charge of AlO_4^- groups in the structure of geopolymer gel. Geopolymers heated up to 900 °C had the same physical aspect as the initial ones and around 1000 °C, the samples warped and were glazed, blistered and consisted of cracks. When geopolymers were heated, new crystalline phases generally appeared around 900 °C. The microstructure of the geopolymers cured up to 90 °C contained pores but was consolidated enough to give high compressive strength. Conversely, the microstructure of geopolymers heated between 300 and 900 °C was progressively damaged and peeled which provoked decrease of compressive strength. Hence, heating metakaolin-based geopolymers at elevated temperatures provokes decrease of the characteristics of fired products as a result of elimination of the water which forms hydration spheres around the compensating cations (Na^+) opposed to tetrahedral groups AlO_4^- along with transformation of the geopolymer gel.

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